



Europäisches Patentamt
European Patent Office
Office européen des brevets

(19)

(11) Publication number:

0 164 881
A1

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 85303191.2

(51) Int. Cl.⁴: **B 01 D 53/36**
B 01 J 23/68

(22) Date of filing: 03.05.85

(30) Priority: 04.05.84 US 607048

(43) Date of publication of application:
18.12.85 Bulletin 85/51

(84) Designated Contracting States:
AT BE CH DE FR GB IT LI LU NL SE

(71) Applicant: **ENGELHARD CORPORATION**
70 Wood Avenue South CN 770
Iselin New Jersey 08830(US)

(72) Inventor: **Hartwig, Michael M.**
44 Rolling Hill Drive
Chatham New Jersey(US)

(74) Representative: **Colgan, Stephen James et al,**
CARPMAELS & RANSFORD 43 Bloomsbury Square
London WC1A 2RA.(GB)

(54) **Platinum/silver vanadate catalyzed diesel exhaust particulate filter.**

(57) A self-cleaning diesel exhaust particulate filter is disclosed wherein burn-off of collected particulate matter is accomplished at normal exhaust gas temperatures, the filter being provided with a catalyst mixture of a platinum group metal and silver vanadate, the presence of which lowers the temperature at which ignition of the particulate is initiated.

BEST AVAILABLE COPY

EP 0 164 881 A1

Case #: IR/2142

PLATINUM/SILVER VANADATE CATALYZED DIESEL EXHAUST
PARTICULATE FILTER

BACKGROUND OF THE INVENTION

1. Field of the Invention

5 This invention relates to diesel engine exhaust gas treatment and more particularly to the filtering of particulates from diesel engine exhaust gases using a catalyzed filter.

10 2. The Prior Art

 The question of how best to reduce the levels of particulate matter expelled to the atmosphere in the exhaust gases of diesel engines is currently of
15 considerable interest. In this connection, it is desired to develop efficient and practical devices for removing substantial portions of particulates from the exhaust gases in diesel engine exhaust systems before permitting the exhaust gases to escape to the
20 atmosphere.

 It is known in the art to provide diesel engines with an exhaust filter which traps particulates from the exhaust gas stream during engine operation. The filters are generally made of porous, solid

materials having a plurality of pores extending therethrough and having small cross-sectional size, such that the filter is permeable to the exhaust gases which flow through the filters and are capable of restraining most or all of the particulates from passing through the filter with the gas. The restrained particulates consist generally of carbonaceous particulates in the form of soot particles. As the mass of collected particulates increases, the flow rate of the exhaust gas through the filter is usually impeded, whereby an increased back pressure is encountered within the filter and reduced engine efficiency results. At this point, the filter is either discarded as a disposable/replaceable element or removed and regenerated by burning the collected particles off at temperatures in excess of 510°C so that the filter can be reused.

There is a desire in the art to more simply regenerate the particulate filter by continuous burn-off or incineration of the soot particles as they are trapped in the filter. However, experience has shown that in normal diesel engine operation, the temperature in the exhaust system varies substantially under different conditions of engine load and speed and that the temperatures in the filter only occasionally reaches the 510°C temperature level required to incinerate the trapped particulate.

The art, e.g., West German Disclosure Publication DE 3141713 published May 11, 1983, has

attempted to rectify this situation by the use of a filter which embodies a catalytic material which lowers the ignition temperature of the soot particles exposed to the hot exhaust gas stream, the catalyst being
5 composed of silver vanadate on a transition metal oxide carrier such as aluminum oxide, silicon dioxide, titanium dioxide, zirconium dioxide and oxides of rare earth metals. U.S. 4,303,552 teaches a diesel exhaust catalyst comprised of a bulk catalytic material
10 consisting of an element of the first transition series, silver or hafnium, and a noble metal catalyst e.g. platinum, palladium or chromium supported on a porous refractory inorganic oxide such as α -alumina, magnesia and silica.

15 There is a need in the art, and it is therefore an object of the present invention, to effect soot particle burn-off in the diesel engine exhaust particulate filter at normal engine operating exhaust gas temperatures.

20 It is a further object of the invention to provide means whereby the temperature at which soot particles may be incinerated can be lowered to a level more closely approximating the exhaust gas temperatures encountered in normal diesel engine operation whereby
25 burn-off and incineration of the soot particles trapped in the filter may be readily achieved and excessive particulate build-up in the filter avoided without risk of damage to the filter.

SUMMARY OF THE INVENTION

These and other objects of the present invention are obtained by means of a filter device for use in the exhaust system of a diesel engine, wherein a filter element is provided with a catalyst mixture of a platinum group metal and silver vanadate. The presence of the catalyst mixture in the filter lowers the temperature at which ignition and incineration of the particulates collected on the filter walls may be effected so that continuous self-cleaning or regeneration of the filter is accomplished at diesel exhaust gas temperatures encountered under normal diesel engine operating conditions whereby particulate plugging is avoided.

BRIEF DESCRIPTION OF THE DRAWINGS

The present invention may be understood and will hereinafter be explained with reference to the graphs in the Figure, the bars of which show data plotted from simulated diesel engine tests indicating the exhaust gas temperatures at which occurs 20%, 50% and 80% removal of the soot deposited on a Pt/silver vanadate catalyzed exhaust particulate filter prepared in accordance with the present invention, and for comparison purposes, the temperatures at which soot removal occurs with a prior art silver vanadate catalyzed particulate filter, a Pt/MgO catalyzed filter

and an uncatalyzed filter. From the Figure, it is seen that by using a Pt/silver vanadate catalyzed particulate filter in accordance with the present invention, soot removal can be generally effected at
5 lower temperatures when compared to a silver vanadate catalyzed particulate filter, a filter catalyzed with a Pt/MgO combination or an uncatalyzed filter.

DETAILED DESCRIPTION OF THE INVENTION

10

In the practice of the present invention, the Pt/silver vanadate catalyzed filter is placed in the filter housing mounted in the exhaust gas handling system of a diesel engine which includes an exhaust
15 manifold. The filter and filter housing are placed, along with any other exhaust gas line elements which may be present, between the exhaust gas manifold of the engine and the end of the exhaust tailpipe which is open to the atmosphere, but preferably as close as
20 possible to the engine exhaust manifold to benefit from the higher temperature. Within the filter housing is placed the high efficiency, selfregenerating, Pt/silver vanadate catalyzed filter element of the present invention which is adapted to collect particulates in
25 the exhaust gases delivered to the filter housing from the engine manifold. The filter element may be formed of any porous high temperature material which is configured to trap and hold substantial quantities of particulates from the diesel engine exhaust gases with-

out creating an excessive restriction to exhaust gas flow and able to withstand the elevated temperatures encountered in exhaust gases during engine operation.

5 Filter elements which are mounted in the filter housing for filtering diesel engine exhaust particulates include thin, porous-walled honeycomb (monolith) or foam structures through which the exhaust gases pass without causing too great an increase of backpressure or pressure drop across the filter
10 housing. Normally the presence of a clean filter element will create a backpressure or pressure differential of 10 to 100 millibar which does not materially affect the operating efficiency of the diesel engine. These filters are generally fabricated
15 from ceramics, generally crystalline, glass ceramics, glasses, metals, cermets, resins or organic polymers, papers, textile fabrics (with or without fillers) and combinations thereof. A detailed description of the variety of prior art diesel engine exhaust particulate
20 filters which may be catalyzed in accordance with the practice of the present invention is disclosed in U.S. 4,329,162, the disclosure of which is herein incorporated by reference.

In operation, exhaust gases emitted by the
25 diesel engine are passed from the exhaust manifold through the exhaust pipe and the exhaust particulate filter housing wherein is mounted the catalyzed exhaust filter of the present invention. Within the filter, when the engine is cold or at low vehicle speeds, the

exhaust gases pass through the porous walls where substantial portions of the particulates contained in the gases are collected on the catalyzed surfaces of the porous filter medium. At exhaust gas temperatures of about 400-500°C, which temperatures are reached at general operating speeds under normal loads in a typical diesel passenger automobile, the particulate collected on the walls of the filter are ignited and the collected particulate is continuously incinerated at these exhaust temperatures. The cleaned exhaust gas then passes out of the filter to the remaining portions of the exhaust system from which it escapes to the atmosphere.

The catalyst of the present invention is characterized by a mixture of a platinum group metal such as platinum, palladium, rhodium and ruthenium and silver vanadate with a weight ratio between the platinum group metal and the silver vanadate of about 1:4 to about 1:2000 and preferably about 1:20 to about 1:400.

Platinum is the preferred platinum group metal component of the catalyst mixture of the present invention.

In preparing the catalyzed particulate filters of the present invention, the catalyst may be present in the form of a coating or film layer consisting of the mixture of platinum group metal and silver vanadate at a coating weight or concentration of about 100.5 to about 1025 grams per cubic foot (g/ft³)

of unit filter volume of which about 0.5 to about 25g/ft³ is comprised of the platinum group metal and preferably about 2 to about 15g/ft³ and about 100 to about 1000g/ft³ and preferably about 300 to about 800 g/ft³ of the silver vanadate.

Depositing the catalyst mixture of the present invention on the porous walls of a filter element such as a monolithic ceramic material or a foam ceramic material can be carried out in any conventional manner. A preferred method of depositing the catalyst mixture on the surfaces of the filter element walls is to impregnate the filter element with an aqueous suspension of the silver vanadate impregnated with a salt of the platinum group. This is best accomplished by bringing the filter element into contact with an aqueous solution or suspension of either the platinum group metal salt or silver vanadate or both by pouring the solution or suspension into the channels of the filter element, removing excess diluent by draining and subsequent drying at 80° - 150°C followed by calcining at 250° - 600°C.

The present invention is illustrated by the following Example:

25

EXAMPLE

A series of Corning diesel particulate filter elements of 5.6 inch diameter and 6.0 inch length (150.96in³ volume) having a ceramic cordierite monolith

structure of 10-40 micron pore size range, 200 cell/in² cell density and a 25 mil wall thickness was selected for catalyst treatment in the following manner:

355.7 grams of sodium vanadate ($\text{NaVO}_3 \cdot 4\text{H}_2\text{O}$) were dissolved in 3.2 liters deionized water, heated to 75°C and then 271.2 grams AgNO_3 in 250 cc water was slowly added with stirring. Orange colored silver monovanadate immediately precipitated. The precipitate was washed, filtered and then dried at 80°C.

129g of the silver monovanadate obtained above was impregnated, to incipient wetness, with an aqueous salt of a platinum group metal containing 1.91g of platinum metal. The mixture was stirred for 5 minutes. 5 ml of actic acid was then added, and the mixture stirred for an additional 5 minutes. The platinum impregnated silver monovanadate was then washed with a total of 1378 g H_2O filtered by suction and dried at 110°C.

The platinum impregnated silver monovanadate obtained above was suspended in 400 ml H_2O and ball milled for 15 hours. The ball milled platinum impregnated silver monovanadate was diluted to 1.5 liter with deionized water. The resulting suspension was then poured into the channels of the filter element, excess slurry was removed from the filter element. The filter element was calcined at 300°C for 3 hours. The cooled filter element was determined to contain 9.7g/ft³ platinum and 657g/ft³ silver vanadate.

The so catalyzed filter element was weighed and then placed in a filter housing exposed to the exhaust stream of a Daimler-Benz diesel engine. After a back pressure of 0.7 bar had built up in the exhaust gas stream, the filter elements were weighed and then placed in reactors heated to different temperatures, e.g. 500°C, 550°C, and 635°C. The weight loss in the filter element was then determined. These data are recorded in The Figure as the temperature at which 20% (A) 50% (B) and 80% (C) of the captured soot was burned off the particulate filter.

For the purposes of comparison, the procedure of the Example was repeated with the exception that the temperatures at which 20%, 50%, and 80% soot removal was obtained for a ceramic monolith filter element which had been catalyzed, with 589g/ft³ silver vanadate designated by the symbol "C₁", a ceramic monolith filter which had been catalyzed with a combination of platinum and magnesium oxide (designated by the symbol "C₂") the amount of Pt catalyst present on the filter being about 50g/ft³. and a filter element that had not been catalyzed, designated "C₃". The temperature data for filters C₁, C₂ and C₃ are also recorded in the Figure.

The Figure shows a graph wherein the temperatures at which 20%, 50% and 80% of the soot deposited on the particulate filters is burned off is plotted on the vertical axis. The bars are plotted from actual data. The Figure illustrates graphically

that by using a Pt/silver vanadate filter element, burn-off of the soot had occurred at lower temperatures when compared to the silver vanadate catalyzed filter element (C_1) or the filter element catalyzed with a platinum/MgO catalyst (C_2) or the uncatalyzed filter
5 element (C_3).

While specific components of the present system are defined above, many other variables may be introduced which may in any way affect, enhance or
10 otherwise improve the system of the present invention. These are intended to be included herein.

Although variations are shown in the present application, many modifications and ramifications will occur to those skilled in the art upon a reading of the
15 present disclosure. These, too, are intended to be included herein.

CLAIMS

1. A diesel exhaust particulate filter comprising a high temperature resistant filter element having porous walls adapted to filter particulates present in the exhaust gases of diesel engines and collect the particulates from the gases flowed through the element on the surfaces of the porous walls, the surfaces of the walls having been first provided with a catalyst comprised of a mixture of a platinum group metal and silver vanadate, which catalyst mixture lowers the temperature at which the collected particulates are ignited and combustion thereof initiated, whereby the particulates are continuously removed by burning at the temperature of the exhaust gases with relatively high efficiency and low pressure drop.

2. The filter as defined in Claim 1 wherein the filter is formed of a ceramic material.

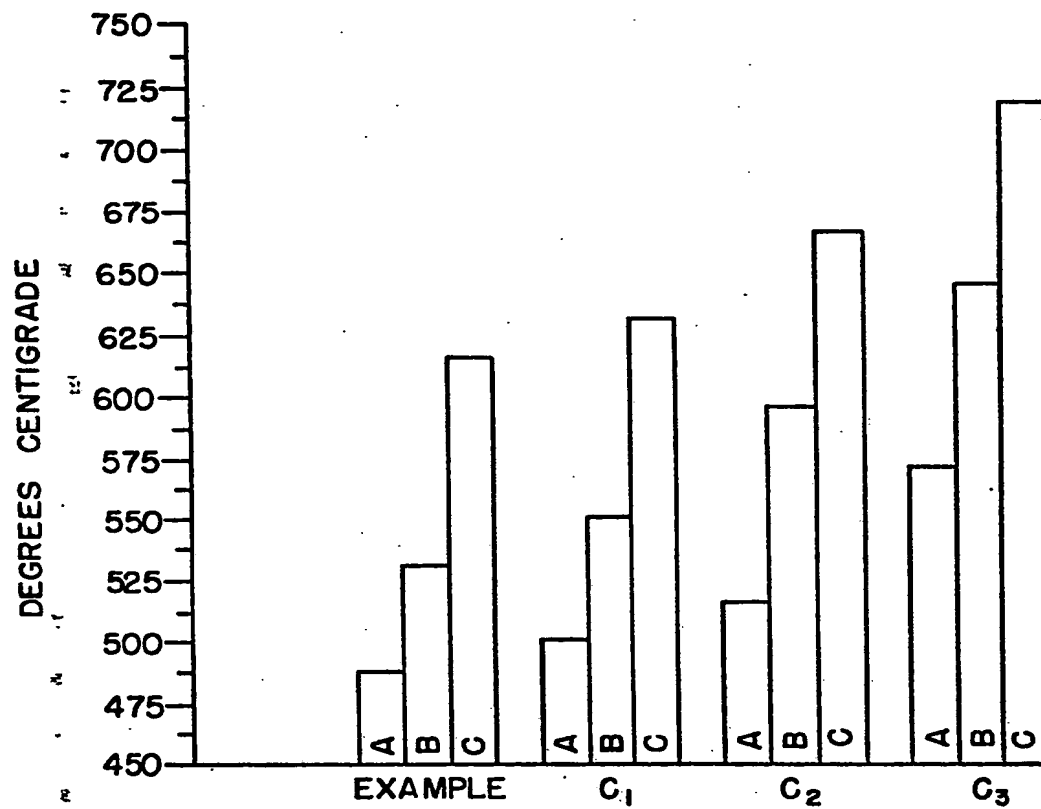
3. The filter as defined in Claim 2 wherein the filter is formed of a ceramic monolithic material.

4. The filter as defined in/^{any preceding} Claim wherein the platinum group metal is platinum.

any preceding
5. The filter as defined in/Claim wherein
the platinum/^{group}metal is present on the surface of the
filter at a concentration of about 0.5 to about 25
grams per square foot of filter surface.

any preceding
6. The filter as defined in/Claim wherein
the silver vanadate is present on the surface of the
filter at a concentration of about 100 to about 1000
grams per square foot of filter surface.

FIG. 1.



FILTER:

A = 20 % BURNOFF
B = 50 % BURNOFF
C = 80 % BURNOFF



European Patent
Office

EUROPEAN SEARCH REPORT

0164881
Application number

EP 85 30 3191

| DOCUMENTS CONSIDERED TO BE RELEVANT | | | |
|---|---|--|---|
| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int. Cl.4) |
| A | EP-A-0 077 524 (DEGUSSA AG) * Claims 1-3; example 2 * | 1-3,6 | B 01 D 53/36 B 01 J 23/68 |
| A | --- PATENT ABSTRACTS OF JAPAN, vol. 8, no. 7, 12 January 1984, page (C-204)(1444); & JP-A-58-174236 (BRIDGESTONE TIRE K.K.) 13-10-1983 ----- | 1,4 | |
| | | | TECHNICAL FIELDS SEARCHED (Int. Cl.4) |
| | | | B 01 D 53/00 B 01 J 23/00 |
| The present search report has been drawn up for all claims | | | |
| Place of search BERLIN | | Date of completion of the search 12-08-1985 | Examiner BERTRAM H E H |
| CATEGORY OF CITED DOCUMENTS | | | |
| X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document | | T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document | |

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☒ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.